

Physical Evaluation of Cleaning Performance – We Are Only Fooling Ourselves
Earl Pratz
Lockheed Martin Space Systems Company, Michoud Operations
13800 Old Gentilly Rd.
New Orleans, LA 70189
504.257.1761
earl.h.pratz@maf.nasa.gov

Abstract

Surface cleaning processes are normally evaluated using visual physical properties such as discolorations, streaking, staining and water-break-free conditions. There is an assumption that these physical methods will evaluate all surfaces all the time for all subsequent operations. We have found that these physical methods are lacking in sensitivity and selectivity with regard to surface residues and subsequent process performance. We will report several conditions where evaluations using visual physical properties are lacking. We will identify possible alternative methods and future needs for surface evaluations.

Introduction

Historical usage of physical properties such as water-break-free, color, and others has given the cleaning practitioner confidence in the performance of the cleaning system. That confidence is borne out through the successful performance of the final steps in the process. The advent of severe environmental restrictions on cleaning materials has led to changes in processing methods including the hardware and chemicals used. With these changes have come changes in the performance of the cleaning processes that have confounded the physical methods used to evaluate cleaning process performance. This paper will present contrasting features of physical and instrumental methods of cleaning performance evaluation and pose goals for the future.

Physical Evaluations

Traditional physical evaluations have included but not been limited to colors, reflected light evaluations, nonvolatile residues (NVR), wipe tests, and water contact angle (water break free) among others. Each technique has its appropriate applicability. Most are dependent on the operator to make judgement of the outcome of the testing.

Colors can indicate many conditions from successful processing to upsets that will produce unsightly surfaces to failures in successive processes. Colors in themselves display conditions that might not be acceptable but as observers, we have difficulty differentiating among shades of color with enough discrimination to determine differing conditions.

The use of reflected light as a measurement method has limitations. The light can relate surface conditions that display situations that enhance performance. It can also mask effects that could deter from acceptable conditions. Particulate contamination is an area where reflected light is used most frequently. However, limited visual resolution of particles by the user can lead to poor interpretation and unacceptable performance.

Nonvolatile residue (NVR) is a means to determine surface condition on a more objective basis than visual acuity. There is a presumption that measured NVR will reflect the cleanliness of a surface. The basic premise is that surface contaminants will dissolve in the test solvent and the result will display a measure of quality. The fallacy is that whatever contaminant is present will have infinite solubility in the test solvent when in actuality the soil might be completely insoluble. This condition could lead to undefined process or performance failures.

The water break free evaluation has been used as an analytical method in innumerable applications from home evaluations of cleanliness to formalized testing (MIL-F-18264). In all cases the test is applied to a surface with the presumption that water forming a continuous film over the surface displays a surface that is "clean" and will perform adequately in succeeding process steps. The water-break-free surface can be produced by conditions where the surface is less than pristine.

Surface Evaluation

Objective surface evaluations require a method to unequivocally determine the composition of the sample. X-ray Photoelectron Spectroscopy or XPS is an analytical technique that can provide surface composition of all materials compatible with vacuum. XPS qualitates and quantitates elements and molecules on the surface of the specimen.

Figure 1: XPS Spectrum of aluminum alloy 2219 surface after deoxidation

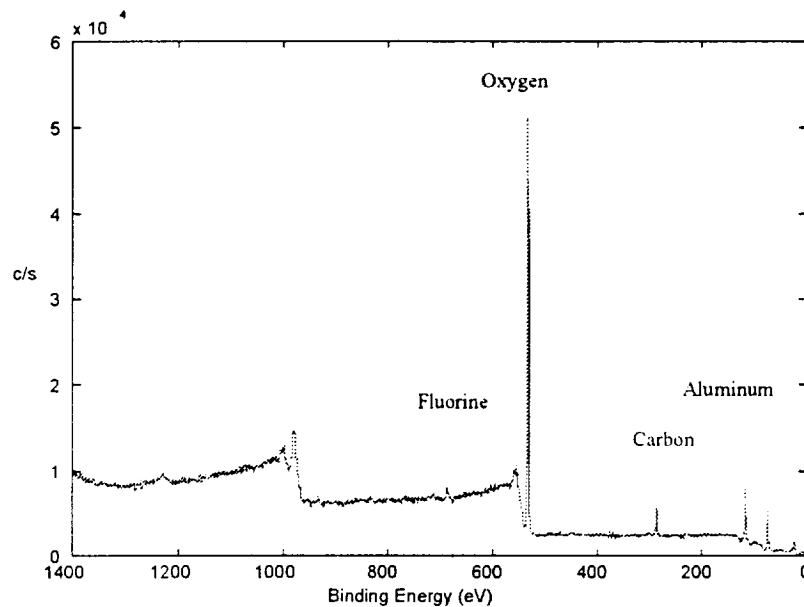
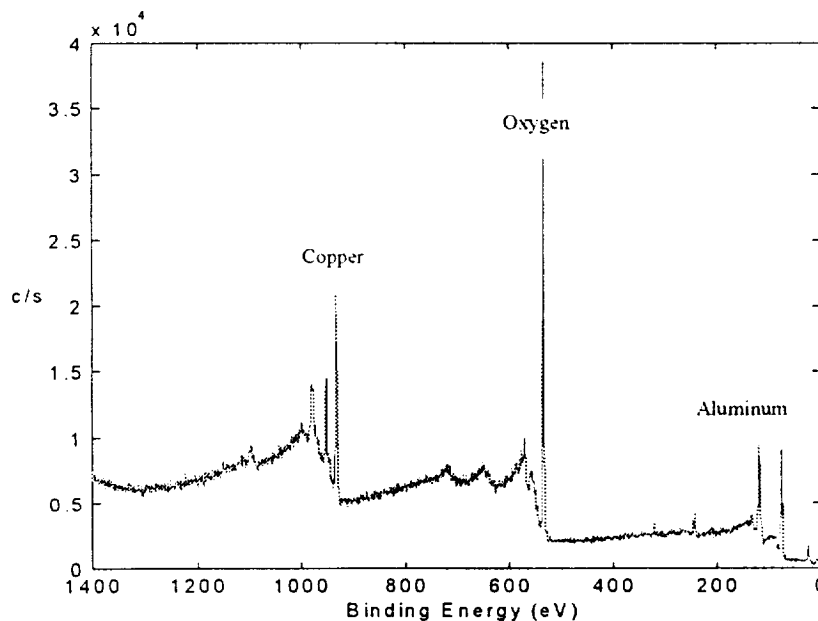


Figure 2: Copper stain on aluminum alloy 2219



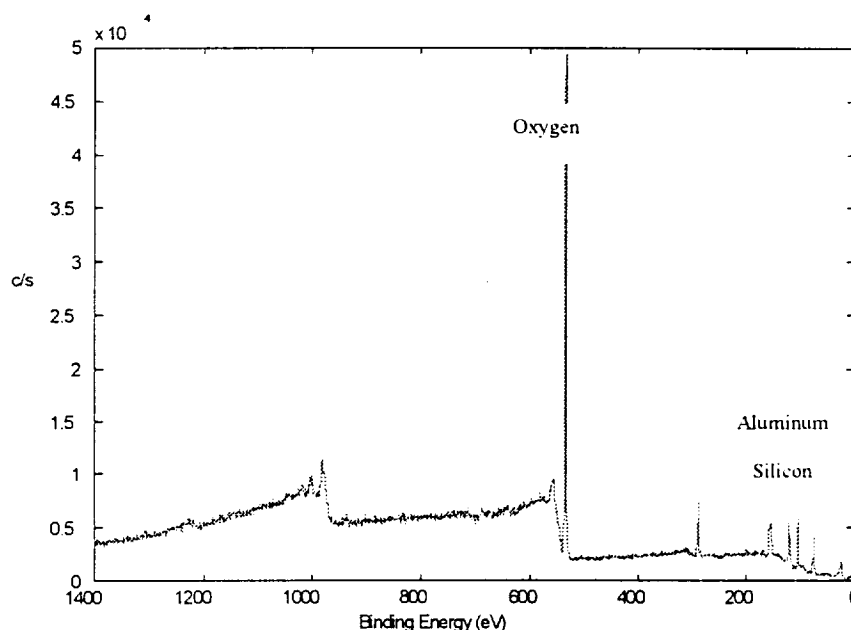
spectrum of an aluminum alloy 2219 panel with a brown stain. The primary elements are iron, oxygen, and aluminum. In all three spectra in figures 2, 3, and 4, the surface color of the panel was brown but the composition of the surface contained different elements that contributed color to the surface. To use visual perception as a means to interpret the results of process variation causing these conditions can lead to incorrect interpretations and improper process changes to accommodate the upset.

Water-break-free Evaluation

Cleanliness evaluation performed by water-break-free testing presumes that evaluated surfaces will display discontinuities in the water film if contamination is present. The corollary is that clean surfaces will present a continuous water film if clean. Figure 1 presents a clean aluminum alloy 2219 surface after acid deoxidation with Oakite LNC and stored in kraft paper. Immediately after cleaning, this surface displayed a water-break-free condition. The surface becomes non water-break-free after a period of storage in kraft paper. There is no evidence of contamination. This would imply a change in the structure of the aluminum oxide surface.

Replacing environmentally insulating cleaning chemicals with more benign materials follows a normal progression where the new material is tested to the same requirements as the old product. Aqueous cleaners are usually expected to produce a water-break-free surface. Our recent testing with an alternate alkaline cleaner has produced interesting results. Figure 5 displays the XPS spectrum of the test surface after contact with the candidate cleaner rinsing with demineralized water. The surface in Figure 5 contains oxygen, aluminum, and silicon.

Figure 5: Aluminum alloy 2219 surface with cleaning residue. Surface was water-break-free.



This condition presented a water-break-free, visually clean condition. Unlike the control of Figure 1, the test surface contains contamination (silicon as silicate) with unknown effects on future processes. Visual evaluation of the surface would have concluded that the surface was acceptable.

Primer Performance on Visually Clean, Contaminated Surfaces

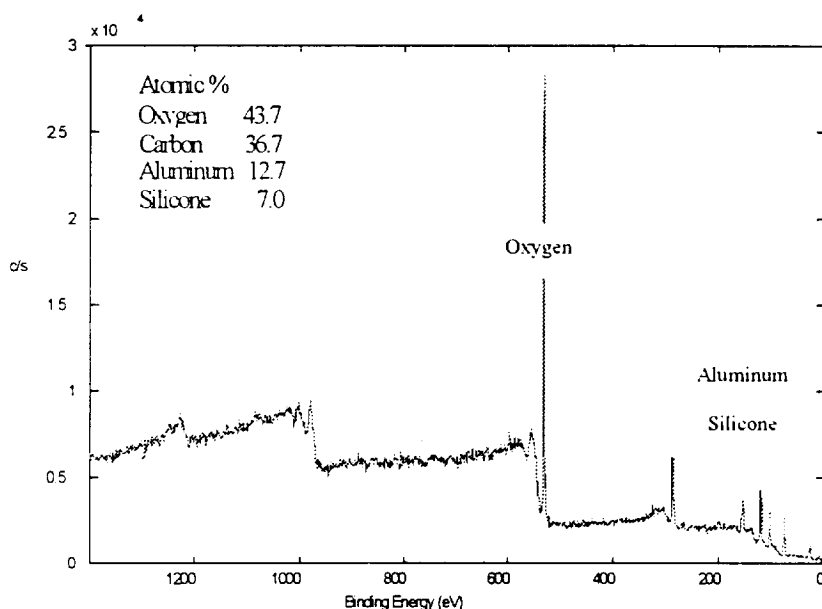
Primer coatings are important for various reasons including surface preparation for topcoat application and corrosion prevention. Historically, primers have been formulated with organic compounds as the solvent but environmental regulations have redirected the formulators to use water as the solvent. A benefit of high organic content (VOC) in primers is the ability of these formulations to accommodate a variety of surface contaminants and

perform as designed. We have tested various organic solvents as candidates to remove typical production soils. The discrimination test used in performance evaluation is primer adhesion. Adhesion is measured in two ways: tensile strength and wet tape adhesion.

The tensile test is performed by adhering a flathead bolt to the primer surface and pulling it from the surface. The force required to remove the bolt is a measure of primer strength. The failure can take place at the adhesive-primer interface or at the primer-substrate interface or a combination of the two. Failure at the primer-substrate implies poor primer adhesion. The wet tape adhesion test examines the result of applying tape to the surface of the primer and quickly removing it. This test is performed after the primer specimen has been immersed in water for 24 hours. Primer removal implies poor primer adhesion.

Surface composition prior to primer application was measured by XPS to determine the level of cleanliness prior to primer application. Figure 6 displays the result of a handwipe cleaning using MEK against an uncured RTV silicone as a target soil. The cleaning was a two-handed wipe and used two wipe passes to remove the soil. The major constituents on the surface are oxygen, carbon, aluminum, and silicon (as silicone). The sample was visually clean at the completion of the cleaning process. Subsequent primer application and testing passed with typical results. The 7.0 atomic percent silicone present did not affect primer performance.

Figure 6: XPS spectrum of MEK/RTV Solvent/Soil Pair Surface



A second set of solvent/soil tests using Dynasolve DS -108 and the same RTV as in the previous test was performed. The visual observation made of the surface after the cleaning operation noted a visually clean surface after three repetitions of the wiping process. The subsequent primer application was unsuccessful. The primer would not adhere to the surface. The XPS analysis of the surface is displayed in Figure 7. Silicone was present at a concentration of 19.0 atomic percent. The quantity of RTV remaining inhibited the primer surface contact.

Data in the previous section has emphasized how visual cleanliness can be deceptive in evaluating performance when no evidence is present of the contaminant. The reverse condition can also exist where contamination is visible but does not reduce performance levels in subsequent processing. Figure 8 is an XPS spectrum of a solvent/soil pair that produced a surface that was heavily soiled with hydrocarbons. So much so that no aluminum from the substrate was evident. This surface was judged by visual evaluation to possess medium streaking. The primer application process was performed to determine if this level of contamination would inhibit performance. As mentioned earlier the organic solvent in the primer was capable of dissolving some contaminants and in this case, the primer performed to expectations even with a heavy carbon load on the surface.

Figure 7: XPS spectra of Primer-bond inhibiting surface containing silicone

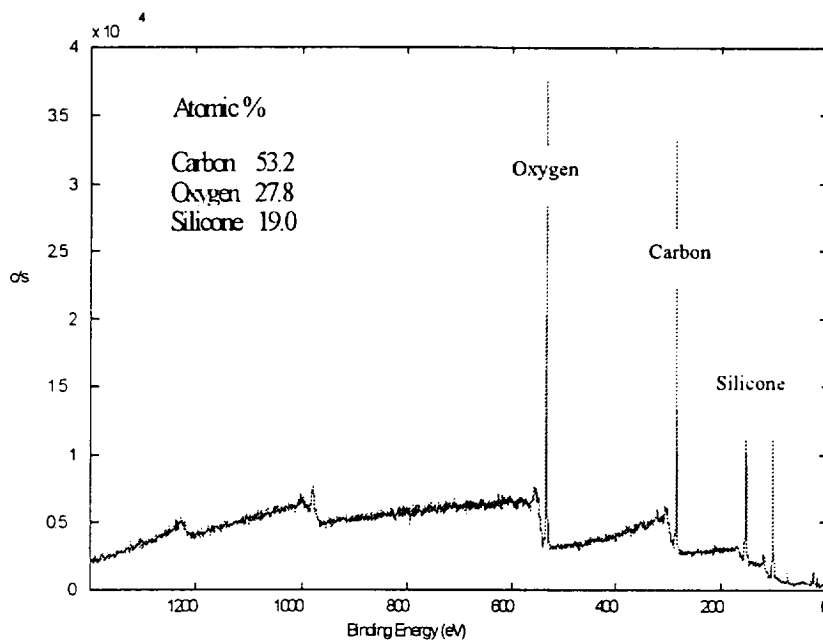
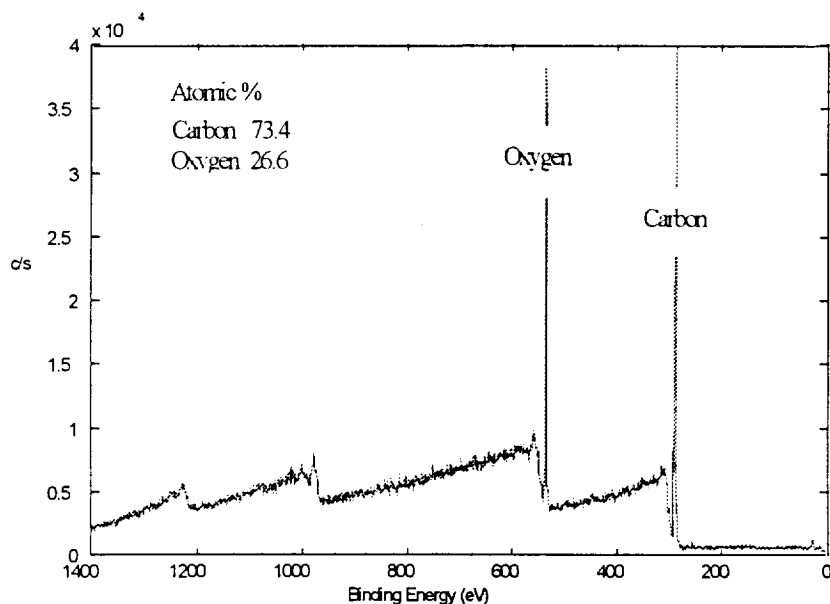


Figure 8: XPS spectra of surface containing high carbon load



Alternative Methods

From the previous data, there is evidence that prior practices used in the evaluation of surface cleanliness lacked sensitivity and specificity. The success of processes was a combination of well-formulated products and flexible process control. Since formulations and processes need change to accommodate more environmentally friendly products, there is a need to recognize the shortcomings of our current practices and move toward more robust sampling and testing to assure that the changes will be successful.

XPS, the analytical method presented in this report is a highly complex technique capable of determining the composition of surfaces. The sample has to be reduced in dimension, which can be problematic. However, XPS can be applied to production monitoring by using surrogate specimens but is not a necessity. Other analytical methods

can be used that remove operator influence in interpretation. The most important concern in surface evaluation is to reduce operator interpretation and provide either a "go-no go" response or a measured response that relates to the soil expected or the condition desired.

Insitu surface analysis methods focus primarily on the use of non-contact methods to excite the sample and collect data. Some soils contain contaminants that will absorb ultraviolet (UV) light and reemit it at a different wavelength visible to the eye. This "fluorescence" can be used to determine contamination but has two shortcomings. The soil must contain a fluorescing contaminant, the operator must make a decision as to the level of contamination, and whether it is acceptable. This again requires interpretation on the operators part.

Another method that uses UV light is Optically Stimulated Electron Emission or OSEE. OSEE utilizes UV light to stimulate metallic substrates to emit a photoelectron. Attenuation of the signal by surface soils indicates contamination. Limitations to the technique restrict the method to specific substrates.

Another method utilizing light is infrared reflection. Surfaces are exposed to infrared wavelengths. The incident light is directed to the specimen surface and reflected light from the surface is analyzed. The technique is sensitive to most organic-containing soils which allows some discrimination. The method is insensitive to inorganic soils and might not have sensitivity at levels adequate for some inspections.

Chromometers use visible light reflected from a surface similar to infrared reflection to evaluate colors on surfaces. These instruments can be applied to surfaces that are not inherently colored but are susceptible to insensitivity and would not be appropriate for sampling very low level soils.

Cleanliness verifications using solvents are excellent methods for surface evaluations but require appropriate solvents for soils, are limited to areas where sampling is straightforward, and where solvent compatibility is not an issue. The nonvolatile Residue (NVR) method is widely used to detect surface contamination where solvents are used to capture surface soils.

An automated method using solvents is contact angle measurement. This technique uses the interaction of liquids with surfaces to measure wetting. The angle formed between liquid droplet and surface can be quantitated and used as a measure of surface cleanliness quality. Automated instruments are available that can expose surfaces to multiple solvents to judge contact angle from solvents of differing surface tension. This technique is restricted to flat surfaces and surrogate samples if the part is too large to be accommodated by the instrument.

Future Needs

As environmental restrictions cause more changes in processing, verification methods need to be more accurate and flexible to accommodate new situations. As has been seen in the data presented above operator assessment of cleanliness can be misleading or incorrect especially when new products are applied to old processes. Some of the challenges facing surface cleanliness validations include some of the following situations.

Validation of surfaces requires confidence that all areas are inspected. Large areas pose problems since 100 percent inspection using current instrumental methods would be time-consuming or impossible. Rapid, sensitive validation methods need to be identified or developed. On the other end of the spectrum, inspecting small areas is also a challenge since compatible solvents for NVR flushing might be restricted. This might lead to complex multistep processes that add the possibility of contamination to the surfaces under examination.

Engineering technology is changing the breadth of materials that are used in construction. Cleanliness confirmation of diverse surfaces challenges all those involved. Issues in test solution compatibility, instrumental responses caused by high background, and subsequent processing requirements bring significant problems and challenges to cleanliness verification of new materials.

Environmental restrictions placed on organic solvents such as hazardous air pollutant (HAP) reduction, volatile organic carbon (VOC) reduction, and ozone depletion elimination lead cleaning processes toward aqueous-based processes. In replacing organic-based materials with aqueous-based materials in the same process, cleaning verification requires examination. Effort needs to be spent to determine if the prior verification practice will detect new soils contributed by the cleaning process and reflect a surface ready for subsequent processing.